

TECHNOLOGIES OF COAL FLY ASH PROCESSING INTO METALLURGICAL AND SILICATE CHEMICAL PRODUCTS

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ABSTRACT

A study and industrial testing have made for the recovery of aluminum, iron and silica from coal ash, produced by utilities. Alkaline technologies for coal fly ash processing were developed that made it possible to separate the main components of fly ash (SiO_2 , Al_2O_3 , Fe_2O_3) and utilize them separately, producing a large variety of useful products. Some of these technologies have already been successfully tested in pilot programs.

INTRODUCTION

The problem of effective utilization of solid waste from coal-fired power plants is of great importance to many countries. The coal burning utilities of the former Soviet Union generate more than 100 million tons of solid combustion by-products each year. Approximately 1 billion tons of solid waste from utilities is placed in storage and disposal areas. The combustion of coal by utilities in the United States results in the production of over 80 million tons of solid by-products each year yet less than a quarter of coal ash is presently being utilized [1].

The various fields of fly ash application are known [1-3]. In the former Soviet Union much attention has been given to the area of research that is called 'High Technology Ash Application' in the United States [1]. This research focuses on the development of technologies for ash processing with recovery of valuable minerals and metals in particular for the recovery of aluminum. The necessity of this research is caused by the need to find new ways for the utilization of fly and bottom ash and simultaneously to solve the problem of expanding the source of raw materials used in aluminum industry.

Ash contains approximately 1.5-2 times less aluminum oxide than common aluminum raw materials (20-35% Al_2O_3 in ash as compared to 50-62% Al_2O_3 in bauxite). The high level of silica in ashes (40-65% SiO_2) makes it impossible to process them by the easiest and the most economical Bayer method and by the other methods of direct alkaline alumina extraction. Therefore for ash processing other methods are studied: acid, thermal, thermal reducing, electrothermal melting, new alkaline methods.

This paper is dedicated to the development of alkaline methods of ash processing. The laboratory research of alkaline methods of fly ash processing have been done at the Problem Laboratory of Recovery of Light and Rare Metals (Kazakh Politechnical University, Alma-Ata). Large-scale testing of the alkaline technologies has been conducted at the pilot plants of the All-Union Aluminum-Magnesium Institute (VAMI, St.Petersburg), State Research and Designed Cement Institute (GIPROcement, St.Peterburg), and the Institute of General and Inorganic Chemistry (Erevan).

EXPERIMENTAL

Chemical and Mineralogical Description of Ash Samples

Chemical analysis of typical fly ash derived from Ekibastuz coal are given in Table 1.

Table 1
CHEMICAL ANALYSIS (Wt.%) OF FLY ASH

Power Plant	C o n s t i t u e n t									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI	Total
Pavlodar	59.82	27.79	5.48	1.65	1.20	0.72	0.40	0.62	4.50	97.68
Emak	60.50	27.20	5.05	1.90	1.60	0.58	0.30	0.60	4.00	97.73
Troitsk	58.48	30.21	4.78	1.95	1.12	0.66	0.30	0.55	0.80	98.05

The major constituents of the Ekibastuz ashes are silicon dioxide, aluminum oxide and iron oxide which represent about 90-94% of the total. Ekibastuz fly ash is characterized by low content of Na_2O and K_2O ($\leq 1\%$) and CaO and MgO (1.78-2.2).

The mineral part of Ekibastuz coal is represented by kaolinite (60-68%), quartz (27-30%), sider-

ite (3-4%), calcite (2.5-3%), magnesite (1-1.5%) and gyps (0.3-0.5%). At burning of coal the mineral part of it is subjected to a short termed influence of high temperatures, which results in kaolinite decomposition, formation of mullite and glassy phase, thermal dissociation of carbonate, polymorphous conversion of quartz into high temperature modification of silica. All these transformations predetermine the mineralogical composition of ash (Table 2).

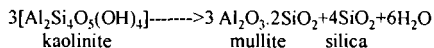
Table 2
MINERALOGICAL ANALYSIS OF SILICON AND
ALUMINUM CONTAINING MINERALS IN EKIBASTUZ ASH

Name	Mineral in Ash	Mass. % Crystal Optics	A n a l y s i s X-Ray Diffraction d, Å	IR-spectroscopy ν , cm ⁻¹
Mulite	30-35	$n_g=1.666$, $n_p=1.654$ $n_g - n_p = 0.012$	5.45; 3.41; 3.36; 2.88; 2.55; 2.21;	*
Glassy Phase	48-51	1. N=1.503 2. N=1.534-1.539	Amorphous Amorphous	1100-1050; 780; 475;
Quartz	2-10	$N_g=1.544$; $N_p=1.531$	4.27; 3.78; 2.44 2.28; 2.23; 1.82	1160; 1095; 800-790; 465;
High Temperature Silica	0-45	No=1.486; Ne=1.454 No - Ne = 0.002	4.09 (intensive); 2.51; 2.88	1160; 1100; 975; 820;

* The absorption regions of mullite appear after dissolving the uncombined silica of ash.

As it follows from Table 2 Ekibastuz ash basically consists of glassy phase (SiO_2 and SiO_2 with admixtures), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and quartz (SiO_2). Well calcinated ash (Troitsk) contains a high temperature crystalline modification of silica with properties close to cristobalite.

Most important for the alkaline methods of ash processing is the process of kaolinite decomposition with the formation of mullite and the isolation of the most part of silica in an uncombined (free) form. This process is described by the summary reaction:



As a result of this reaction aluminum is concentrated in mullite and about 67% of the kaolinite silica is isolated in a free form. Together with silica of quartz and its high-temperature modifications about 70–80% of silica is contained in the ash in the free form. This creates the necessary prerequisites for aluminum oxide and silicon dioxide separation. Stated phase separation of aluminum oxide and silicon dioxide in ashes came to be a basis for research and the development of alkaline methods for ash processing [4].

Interaction between Ash Minerals and Alkaline Solutions

According to the data of mineralogical analysis (Table 2) mullite, glassy phase, quartz and its high temperature modification-crystalite are the main aluminum and silicon containing ash minerals. The comparison of these minerals dissolubility in the alkaline solution is shown in Figure 1.

The comparison of the curves (Figure 1) shows that mullite (1) and quartz (2) have a small dissolubility in alkaline solution while cristobalite (5) dissolves practically completely after 4 hours of alkaline treatment at 105°C [5]. The glassy phase (3) also has good dissolubility in alkaline solution. Its presence and dissolution are determined by a comparison of IR-spectra of ash (Figure 2) and its residue after alkaline treatment.

IR-spectra of ash (Figure 2.1) contain the absorption regions 1100 and 800-780 cm^{-1} which are the characteristic regions of silicates like quartz, cristobalite, and amorphous silica with three-dimensional tetrahedrons of SiO_4 frame. In the IR-spectra of residue after ash alkaline treatment (2) the regions of quartz, glass and cristobalite have completely or partially disappeared and absorption regions of mullite (1180, 970-920, 880-850 cm^{-1}) have appeared.

XRD analysis of residue after alkaline ash treatment reveals the complete disappearance of

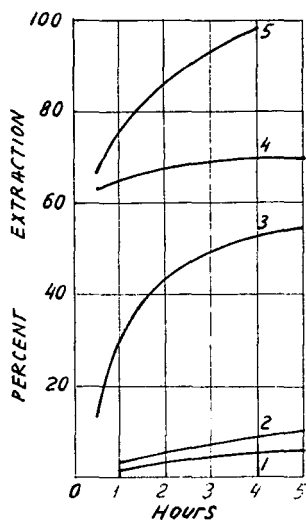


Figure 1. Interaction between alkaline solution and ash compounds: 1 - mulite; 2 - quartz; 3 - ash glassy phase; 4 - ash cristobalite; 5 - synthesized cristobalite.

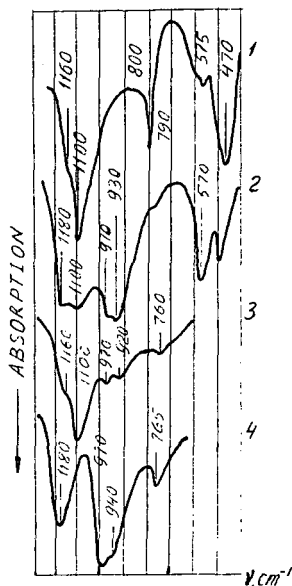


Figure 2. Infra-red Spectra: 1 - ash; 2 - its residue; 3 - ash calcinated at 1250°C; 4 - its residue.

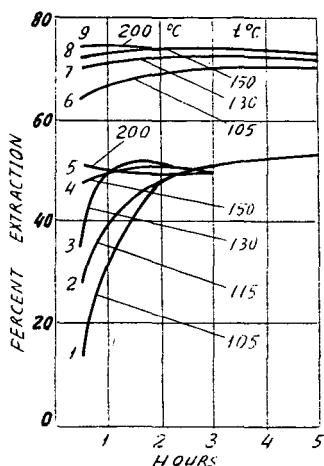
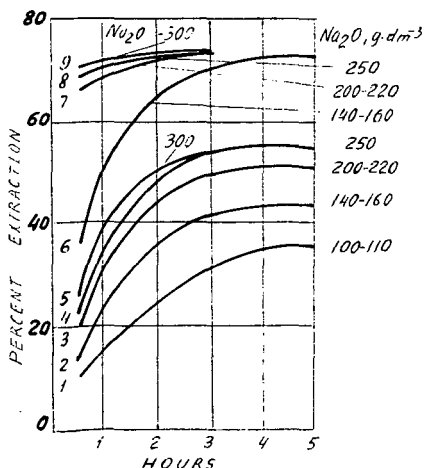


Figure 3. Silica extraction from Fly Ash

crystalobalite maxima $d, \text{\AA}$: 4.09-4.10; 4.52; 3.51 which is well coordinated with the data of crystalobalite alkaline dissolubility (Figure 1). The aforementioned data of chemical, XRD, and IR-spectroscopy research shows that uncombined (free) ash silica is extracted from ash by the alkaline solution.

Hydroalkaline Recovery of Silica from Fly Ash

The influence of various factors on the percentage of silica extraction from fly ash is shown in Figure 3.

The data in Figure 3 shows that free silica is extracted from ash at low rates (temperature 105°C for a duration of 3-4 hours). The process can be realized at atmospheric pressure. The essential augmentation of silica recovery has been reached by means of ash activation which increased the efficiency of silica extraction by 12-20% (Figure 3, curves 6-9).

The intermediates after ash hydroalkaline treatment were the silica alkaline solution (SAS) and the solid residue enriched by aluminum oxide (concentrate of alumina). Chemical composition of SAS, g dm^{-3} : $\text{Na}_2\text{O}=160-220$; $\text{SiO}_2=100-250$; $\text{Al}_2\text{O}_3=2-7$; $\text{Fe}_2\text{O}_3=0.1-0.9$. Concentrate of alumina included %: 44-55 Al_2O_3 ; 30-27 SiO_2 ; 5.5-10 Fe_2O_3 .

Recovery of Iron from Fly Ash by Magnetic Separation

In a number of studies, magnetic separation was applied as a pre-stage before the main operations of ash treatment[6]. Ekibastuz ash consists of 4-10% Fe (as Fe_2O_3). The possibility of recovering the magnetic fraction from Ekibastuz ash and its classified fractions was shown in [7]. The magnetic fractions after raw ash magnetic separation were rich in Fe (60-62% as Fe_2O_3). Classified fractions contained 57.6-66.4% Fe as Fe_2O_3 . Output of the magnetic fractions was 2.12-5%. The non-magnetic residues were depleted of Fe and contained 2.6-3.6% Fe as Fe_2O_3 .

Technology of Alkaline Fly Ash Processing. The Principle Process Flow Sheet

The described findings of hydroalkaline recovery of silica were taken as a basis for the design of the process flow sheet of fly ash processing into metallurgical, silicate chemical products and building materials. The principle flow sheet (Figure 4) includes the hydroalkaline silica extraction from fly ash. This operation allows one to extract the good part of ash silica (60-77%) into the alkaline solution and then to process it into various silicate chemical products (sodium and calcium metasilicates, sodium-silicate mixtures, amorphous and crystalline silica and others). The solid intermediates from ash extraction-alumina concentrate-can be processed into alumina, aluminum, and aluminates by thermal or hydrochemical alkaline methods or can be used for aluminum-silicon alloys, refractories, and concrete production. Mud of the alumina production is a valuable raw material for cements.

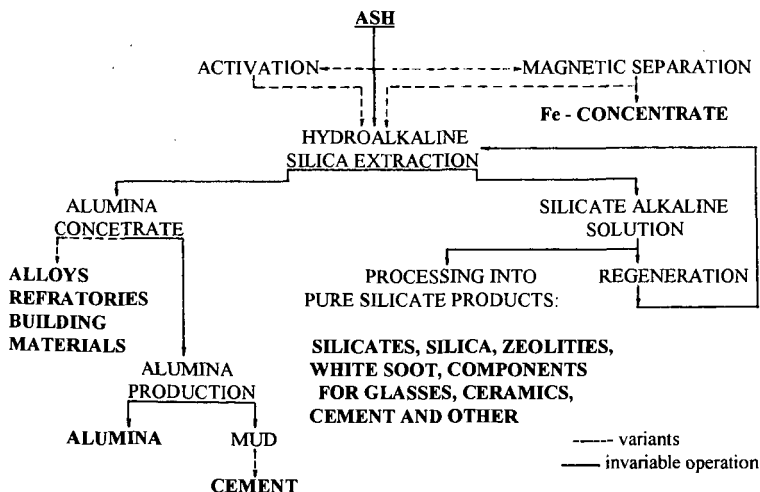


Figure 4. Flow sheet for alumina, silica and iron recovery from ash

Large-Scale Testing of the Alkaline Technologies

Practically all of the main technological operations of the fly ash processing have been tested in pilot programs: ash activation, hydroalkaline silica extraction, settling and filtration of ash pulp, washing of the alumina concentrate, processing it into alumina, producing of portland cement from mud, silica alkaline solutions processing into sodium and calcium metasilicates. Alumina output was made up of 86% Al_2O_3 (90-91.7% at the standard leaching).

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